Article

Variety of Iron Oxide Inclusions in Sapphire from Southern Vietnam: Indication of Environmental Change during Crystallization

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Abstract: Sapphires from alluvial deposits associated with Cenozoic basalts in Southern Vietnam were collected for investigation of mineral inclusions. In this report, primary iron oxide inclusions were focused on, with detailed mineral chemistry using a Raman spectroscope and electron probe micro-analyzer. Consequently, a variety of iron oxide inclusions were recognized as wüstite, hercynite, and ilmenite. Ilmenite falling within an ilmenite–hematite series ranged in composition between $\text{Il}_{24-30}\text{He}_{36-38}\text{Mt}_{35-40}$ and $\text{Il}_{49-54}\text{He}_{34-40}\text{Mt}_{7-10}$, classified as titanomagnetite and titanohematite, respectively. Wüstite with non-stoichiometry, $(\text{Fe}^{2+}_{0.3-0.9})(\text{Ti}^{3+}_{<0.179}\text{Al}^{3+}_{\leq 0.6}\text{Cr}^{3+}_{<0.1}\text{Fe}^{3+}_{\leq 0.46})\square_{\leq 0.23}\text{O}$, was associated with hercynite inclusions, clearly indicating cogenetic sapphire formation. Wüstite and sapphire appear to have been formed from the breakdown reaction of hercynite (hercynite = sapphire + wüstite) within a reduction magma chamber. Titanohematite and titanomagnetite series might have crystallized during iron–titanium reequilibration via subsolidus exsolution under a slightly oxidized cooling process.

Keywords: sapphire; wüstite; hercynite; Cenozoic basalt

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1. Introduction

Iron oxide minerals have been considered as a significant geothermometer for their host rocks [1–6]. Previous investigations of gem sapphire from Southern Vietnam, such as Dak Nong, Di Linh, and Binh Thuan deposits, have reported several iron oxide inclusions [7–9]. Most of these iron oxides were identified as ilmenite, magnetite–hercynite, and chromite–hercynite, using a scanning electron microscope–energy dispersive spectrometer (SEM-EDS) and an X-ray diffractometer (XRD) [8]. Moreover, Izokh et al. [7] reported an iron oxide inclusion, namely, Al–Ti–hematite, that was chemically analyzed by an electron probe micro-analyzer (EPMA); subsequently, they proposed that crystallization of host sapphire should relate to iron-rich syenitic melt and metasomatism between crustal rocks and contaminated basaltic melt in the Dak Nong deposit. Recently, Vu et al. [9] reported spinel and other unidentified oxide inclusions in sapphires from many deposits in Southern Vietnam which more details and further investigation are reported herein this manuscript. Besides, the crystallization of sapphire and related zircon from Southern Vietnam may occur in the lithospheric mantle which is related to carbonatite-dominant melts as a result of partial melting of a metasomatized lithospheric mantle source, at over 900 °C [10].

Although iron oxide inclusions were previously reported, their mineral chemistry has never been fully analyzed. This study was therefore designed to analyze most types of iron oxide inclusion in sapphire from Dak Nong, Di Linh, Binh Thuan, Krong Nang, and Pleiku.

2. Geological Setting

Southern Vietnam geologically consists of a large-scale structure of the Da Lat active continental margin (Da Lat zone), Indosinian polyepisodic orogenic belt (Srepok orogenic belt), and Kontum massif [11], which is part of the Indosinian craton [12] (Figure 1). This region is composed of Archean–Proterozoic basement rocks, Early to Middle Paleozoic cover rocks, Jurassic sediments, late Mesozoic rocks, and Cenozoic basaltic rocks [12] (Figure 2). The basement rocks in this area are characterized by metamorphic complexes of granulites which are usually covered by volcanogenic sedimentary rocks, metamorphosed sedimentary rocks within greenschist facies of the Early to Middle Paleozoic, as well as sandstone, siltstone, and shale of Jurassic sedimentary formation. These basements and upper rocks are intruded by a number of late Mesozoic igneous rocks, including Triassic granite, granodiorite, and granosyenite (results of the Indosinian–Yangtze collision during the Permo-Triassic about 245–240 Ma) and Cretaceous diorite and granodiorite (result of the Paleo-Pacific plate subduction) [13–15]. Late Cenozoic basalts associated with sapphire deposits in Southern Vietnam have been mapped, overlying the older rock formations reported above.

Figure 1. Geological map showing the study area and main tectonic terranes in Southern Vietnam, modified after Tri and Khuc [11] and Hoa et al. [12].

These Late Cenozoic basalts (Figure 2) are related to regional tectonic terranes, particularly after the end of East Sea opening in the Middle Miocene [16–18]. Paleo-Pacific oceanic crustal material, previously subducted into the lower mantle, was subsequently entrained into the Hainan plume which was the main cause of basaltic magmatism in Southern Vietnam [19]. According to Hoang and Flower [20], these volcanic activities were extended more than 100 km in diameter with a thickness up to several hundred meters and covered a total area of approximately 23,000 km². The centers of volcanism appear to have developed during two main eruptive episodes. The early phases generated mainly quartz and olivine tholeiites with rare alkali basalt whereas the later phases produced olivine tholeiite, alkali basalt, basanite, and rare nephelinite. Tholeiite eruptions occurred significantly in the centers associated with extensional rifting. On the other hand, alkali basalt, olivine tholeiite, and basanite appear to have erupted along the conjugate strike-slip faults [18]. It

should be noted that sapphire and zircon occurrences mainly discovered in Quaternary and Upper-Pleistocene alluvial deposits derived from the alkali basalts [8–10,21]. They would originate in the deep-seated formations before being transported as megacryst onto the Earth's surface by alkali basaltic magmas.

Figure 2. Geological map showing alluvial sapphire deposits and associated Cenozoic basalts underlain by the older rock formations in Southern Vietnam, modified after Hoa et al. [12].

3. Materials and Methods

Sapphire collections of about 5 mm crystals were sampled from Dak Nong, Di Linh, Binh Thuan, Krong Nang, and Pleiku in Southern Vietnam (see Figure 2 and Table 1 and Table S1). The sapphire crystals were detected for metallic opaque inclusions for further study. After being mounted in epoxy, they were ground by a diamond wheel until inclusions were exposed; subsequently, they were polished using 6 μm , 3 μm , and 1 μm diamond pastes. These inclusions were initially characterized using a laser Raman spectroscope, inVia model, Renishaw equipped with a Leica optical microscope at the Gem and Jewelry Institute of Thailand (Public Organization) (GIT). The laser beam was generally set at about 5 μm with standard conditions including 532 nm radiation of the NIR diode laser emitting at 785 nm and power of 15.7 mW (about 5 mW on the sample), at a resolution of approximately 0.5 cm^{-1} . It should be noted that Raman patterns of iron minerals may be transformed rapidly by laser induction, leading to the modification of Raman shift, and the same effect can also be induced by the natural processes such as oxidation, recrystallization, order–disorder transitions (cation redistribution), phase transition, or decomposition [22–24]. Therefore, low laser power (0.5 mW) and normal operation power (5 mW) on the sample were applied in this study to observe the Raman pattern and its alteration in wüstite inclusions because its structure is sensitive to laser power. However, ilmenite and hercynite spinel were analyzed using normal operation laser power of 5 mW, as suggested by Wang et al. [25]. Each spectrum was recorded within

the spectral range of 200 cm^{-1} to 1500 cm^{-1} for 20 s of exposure time, 6 accumulation, and $50\times$ magnification, at a laboratory temperature of about $22\text{ }^{\circ}\text{C}$.

After identification using the Raman technique, these inclusion samples were carbon coated prior to major and minor analyses using an electron probe microanalyzer (EPMA, JEOL model JXA-8100) at the Department of Geology, Faculty of Science, Chulalongkorn University. The analytical condition was set at 15 kV acceleration voltages with about 24 nA probe current. Appropriate standards and analytical crystals were selected for analyses with 30 s for peak counts and background counts of each element before automatic ZAF correction, requested for three main effects (i.e., atomic number, absorption, and fluorescence excitation) influencing spectroscopic analysis of characteristic X-rays, was applied to report in oxide contents. Finally, atomic proportions of these analyses were recalculated on the basis of proper oxygen in their formula before Fe^{2+} and Fe^{3+} ratios were estimated accordingly using the equation of Droop [26].

4. Results

Although all of the studied iron oxide minerals looked similarly black opaque crystals, their morphological affinities were classified into two groups, octahedral and rhombohedral shapes, indicating significantly primary inclusions. Octahedral iron oxides formed as single and aggregate crystals ranging in size from $20\text{--}500\text{ }\mu\text{m}$ (Figure 3). In contrast, rhombohedral iron oxides occurred typically as single crystals, about $80\text{--}600\text{ }\mu\text{m}$ long, and $40\text{--}300\text{ }\mu\text{m}$ wide (Figure 4). Raman spectroscopic identification of these iron oxide inclusions is reported below.

Figure 3. Photomicrographs taken with dark field illumination, magnified $50\times$, showing: (a) a small octahedral wüstite inclusion in sapphire (sample DL50) from Di Linh; (b) a small octahedral hercynite inclusion in sapphire (sample KN43) from Krong Nang; (c) aggregate crystals of octahedral wüstite inclusions in sapphire (sample GL27) from Pleiku, and (d) aggregate crystals of octahedral hercynite inclusions in sapphire (sample DN16) from Dak Nong.

Figure 4. Photomicrographs taken with dark field illumination, magnified 50 $\times$, showing rhombohedral ilmenite inclusions: (a) a single crystal (sample DL85 from Di Linh) as reported by Vu et al. [9] and (b) several single crystals (sample GL25 from Pleiku).

Three distinctive types were recognized by Raman spectra, including wüstite, hercynite, and ilmenite groups. In comparison with morphological features, wüstite and hercynite inclusions typically showed octahedral shape in forms of single and aggregate crystals. Moreover, wüstite–hercynite composite inclusions (Figure 5) could be found. On the other hand, ilmenite inclusions were mostly characterized by rhombohedral single crystals.

Figure 5. (a) Photomicrographs and (b) black-scattered electron images (BSIs) showing hercynite–wüstite composite inclusion found in sapphire (sample PT55) from Binh Thuan.

At the low laser power (0.5 mW), all studied wüstite inclusions clearly showed only a sharp peak at 670 cm^{-1} , which closely resembled magnetite spectra (Figure 6a). On the other hand, at high laser power (5 mW), some wüstite inclusions (e.g., DL50, DL56, PT17) showed characteristic patterns of magnetite (weaker peak in the range of 650–670 cm^{-1}), hematite with higher intensity peaks at 218, 285, and 388, and wüstite assigned by the 595 cm^{-1} peak, as suggested by Hanesch [23] (Figure 6b). These spectra were matched well with wüstite spectra observed at low and high laser powers reported by Faria et al. [22]. In addition, some wüstite inclusions showed a broader band in the 650–670 cm^{-1} region (strongest peak at approximately 667 cm^{-1}) of magnetite with higher intensity (Figure 6c).

Figure 6. Raman spectra of wüstite inclusion observed at different laser powers, 0.5 mW (a) and 5 mW (b,c); sample DL50 from Di Linh (a,b) and sample PT49 from Binh Thuan (c).

The Raman spectrum of hercynite is representatively displayed in Figure 7. The spectrum yielded a strong band at 753 cm^{-1} and a weak peak at 701 cm^{-1} which indicate the vibration of AlO_4 tetrahedra, characteristic of a spinel structure, as suggested by Cynn et al. [27]. This spectrum was similar to the hercynite spinel reported by Ospitali et al. [28].

Figure 7. Raman spectrum, measured at 5 mW laser power, of hercynite spinel inclusion in sapphire (sample KN43) from Krong Nang.

An ilmenite inclusion showed Raman characteristics of mixture minerals of which Raman peaks were recognized at 299, 498, and 683 cm^{-1} (Figure 8a). The highest intensity peak, 683 cm^{-1} , was due to ilmenite, as suggested by Wang et al. [25], whereas 299 and 498 cm^{-1} peaks were caused by hematite [22]. Additionally, some ilmenite inclusions revealed broadened peaks at 220, 293, and 613 cm^{-1} which matched well with the hematite's pattern; moreover, an additional characteristic peak of ilmenite was present around 683 cm^{-1} as well as weak peaks at 399, 600, and 1298 cm^{-1} , likely indicating oxidized titanomagnetite (Figure 8b) [24,25]. These different Raman patterns indicated that ilmenite inclusions in this study may have a variety of chemical compositions.

Figure 8. Raman spectra, measured at 5 mW laser power, of ilmenite inclusions showing different patterns as reported in the main text; (a) sample DL85 from Di Linh and (b) sample GL25 from Pleiku.

Mineral chemistry of these iron oxide inclusions, based on the EPMA, clearly supported Raman spectroscopic identification. Representative EPMA analyses of each iron oxide type are shown in Tables 1–3.

Table 1. Representative EPMA analyses of wüstite inclusions in sapphire from Southern Vietnam.

Mineral Phase Analysis (wt%)	Wüstite (FeO)–Hercynite						Wüstite (FeO)			Rumburk ¹	
	Southern Vietnam						Southern Vietnam				Germany
	Dak Nong	Di Linh	Krong Nang	Binh Thuan		Pleiku	Di Linh		Binh Thuan		
	DN74	DL14 *	KN19 *	PT49	PT55a	GL27	DL50 *	DL56	PT17a		
SiO ₂	0.03	0.00	0.06	0.44	0.44	0.34	0.02	0.15	0.27	0.85	
TiO ₂	0.84	1.53	1.24	5.89	0.38	0.00	2.33	3.25	0.22	0.04	
Al ₂ O ₃	9.85	6.66	11.84	12.88	19.28	11.39	0.21	0.27	0.12	0.29	
Cr ₂ O ₃	0.01	0.04	0.03	0.03	0.00	0.03	0.02	0.04	0.03	na	
FeO	88.13	89.29	86.30	77.44	77.44	86.25	96.45	95.31	95.46	91.94	
MnO	0.20	1.49	0.18	2.25	2.25	0.00	0.41	0.35	1.81	0.14	
MgO	0.35	0.29	0.37	0.20	0.23	0.00	1.36	0.40	0.88	0.12	
ZnO	0.67	0.36	0.51	0.30	0.25	0.07	0.00	0.00	0.00	na	
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.29	0.00	0.14	
NiO	0.02	0.00	0.10	0.01	0.02	0.05	0.03	0.00	0.00	na	
Total	100.1	99.66	100.52	99.47	99.90	98.12	100.8	100.1	98.78	93.52	
Formula 4(O)											
Si	0.001	0.000	0.002	0.002	0.002	0.015	0.001	0.007	0.013	0.043	
Ti	0.027	0.051	0.039	0.178	0.011	0.000	0.081	0.113	0.008	0.002	
Al	0.496	0.346	0.580	0.612	0.892	0.577	0.011	0.015	0.007	0.017	
Cr	0.000	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.001		
Fe ²⁺	3.147	3.291	3.001	2.604	2.541	1.507	3.708	3.681	1.962	3.863	
Mn	0.007	0.056	0.006	0.081	0.075	0.000	0.016	0.014	0.073	0.006	
Mg	0.022	0.019	0.023	0.009	0.011	0.000	0.093	0.027	0.062	0.009	
Zn	0.021	0.012	0.016	0.000	0.009	0.002	0.000	0.000	0.000		
Ca	0.000	0.000	0.000	0.024	0.000	0.000	0.000	0.014	0.000	0.008	
Ni	0.001	0.000	0.000	0.003	0.000	0.002	0.001	0.000	0.000		
Total *	3.723	3.776	3.660	3.514	3.541	3.697	3.912	3.872	3.975	3.947	
ΣR ²⁺	3.198	3.378	3.046	2.721	2.636	1.511	3.818	3.736	2.097	3.886	
ΣR ³⁺	0.524	0.397	0.622	0.793	0.545	0.95	0.093	0.135	0.028	0.062	
% wüstite	86	89	83	77	85	84	98	96	99	98	
% hercynite	14	11	17	23	15	16	2	4	1	2	

Note: * previously reported by Vu et al. [9]; ¹ Seifert et al. [29]; na = not analyzed; ΣR²⁺ = Fe²⁺ + Mn + Mg + Zn + Ca + Ni; ΣR³⁺ = Si + Ti + Al + Cr + Fe³⁺.

Table 2. Representative EPMA analyses of hercynite spinel inclusions in sapphire from Southern Vietnam.

Mineral Phase Analysis (wt%)	Dak Nong		Di Linh	Krong Nang		Binh Thuan			Pleiku
	DN12 *	DN16 *	DL62 *	KN20b	KN43	PT07	PT17b	PT55b	GL07
SiO ₂	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.02
TiO ₂	0.12	0.08	0.70	0.00	0.00	0.00	0.27	0.00	0.32
Al ₂ O ₃	60.99	60.93	60.76	61.07	60.68	61.12	61.02	60.94	60.02
Cr ₂ O ₃	0.00	0.00	0.09	0.07	0.02	0.01	0.00	0.00	0.00
FeO	33.99	34.18	33.87	33.84	32.24	33.40	35.38	34.62	33.87
MnO	0.00	0.89	0.34	0.81	0.28	0.06	1.47	0.46	0.98
MgO	4.02	4.29	4.62	4.61	5.26	4.55	0.56	4.07	5.23
ZnO	0.12	0.38	0.18	0.00	0.63	0.67	0.01	0.18	0.00
CaO	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
NiO	0.00	0.00	0.00	0.03	0.00	0.09	0.10	0.00	0.00
Total	99.29	100.74	100.58	100.43	98.81	99.91	99.81	100.27	100.45
Formula 32(O)									
Si	0.000	0.000	0.002	0.000	0.000	0.003	0.003	0.000	0.005
Ti	0.020	0.014	0.117	0.000	0.046	0.000	0.046	0.000	0.054
Al	16.134	15.975	15.886	16.003	16.433	16.071	16.433	16.040	15.763
Cr	0.000	0.000	0.016	0.012	0.000	0.002	0.000	0.000	0.000
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.157
Fe ²⁺	6.380	6.359	6.285	6.292	6.762	6.232	6.762	6.466	6.155
Mn	0.000	0.168	0.064	0.152	0.285	0.012	0.285	0.087	0.186
Mg	1.344	1.421	1.529	1.529	0.191	1.514	0.191	1.355	1.739
Zn	0.020	0.062	0.030	0.000	0.002	0.111	0.002	0.030	0.000
Ca	0.015	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000
Ni	0.000	0.000	0.000	0.006	0.018	0.017	0.018	0.000	0.000
Total *	23.913	23.999	23.929	23.993	23.737	23.960	23.737	23.980	24.059
ΣR ²⁺	7.759	8.010	7.907	7.979	7.259	7.885	7.259	7.940	8.080
ΣR ³⁺	16.154	15.989	16.022	16.014	16.479	16.076	16.479	16.040	15.979

Note: * previously reported by Vu et al. [9]. Fe²⁺ and Fe³⁺ were recalculated from total FeO after the method of Droop [26]. ΣR²⁺ = Fe²⁺ + Mn + Mg + Zn + Ca + Ni. ΣR³⁺ = Si + Ti + Al + Cr + Fe³⁺.

Wüstite varied in composition from about 77–97% FeO, <20% Al₂O₃, and <7% TiO₂ with traces of MnO (Table 1). Based on these compositions, it was mostly characterized by a non-stoichiometric formula. The compositions are similar to wüstite that formed under strongly reducing conditions in Rumburk granite in Germany (Table 1). Recalculated atomic proportions show that the hercynite component (ranging from 1 to 23%) may play an important role in the wüstite composition (Seifert et al. [29], Table 1). Based on the procedure of Smyth et al. [30], the average chemical formula can be expressed for non-stoichiometric wüstite as (Fe²⁺_{0.3–0.9})(Ti³⁺_{<0.179}Al³⁺_{≤0.6}Cr³⁺_{<0.1}Fe³⁺_{≤0.46})□_{≤0.23}O, where □ is deficiency of Fe.

Hercynite spinel inclusions presented narrow compositional ranges of 60–62% Al₂O₃, 32–36% FeO, and ≤5.3% MgO (Table 2). Smith et al. [8] previously reported the composition of hercynite inclusions in Di Linh and Binh Thuan sapphires, based on SEM-EDS analyses, varying between chromite–hercynite and magnetite–hercynite series. EPMA analyses of hercynite inclusions in this study showed an almost pure hercynite composition (Fe²⁺_{6.0–6.8}Mn²⁺_{<0.3}Mg²⁺_{<1.8}Zn²⁺_{<0.2}Ca_{<0.1})(Ti³⁺_{<0.3}Al³⁺_{15.8–16.4}Fe³⁺_{<0.2})O₃₂ (Figure 9). It should be noted again that some hercynite was found in close association with wüstites in sapphire from Binh Thuan (sample PT55, as shown in Figure 5, with EPMA analyses presented in Tables 1 and 2).

Table 3. Representative EPMA analyses of ilmenite inclusions in sapphire from Southern Vietnam.

Mineral Phase Analysis (wt%)	Titanohematite			Titanomagnetite		
	Dak Nong	Di Linh		Pleiku	Pleiku	
	DN39 *	DL23 *	DL85 *	GL28	GL25	GL86
SiO ₂	0.11	0.10	0.00	0.08	0.17	0.09
TiO ₂	34.94	37.08	33.77	34.89	18.48	20.27
Al ₂ O ₃	0.02	1.50	0.58	1.14	3.25	2.37
Cr ₂ O ₃	0.00	0.04	0.12	0.05	0.00	0.04
FeO	61.43	61.58	63.48	63.00	76.12	74.54
MnO	0.14	0.06	0.05	0.09	0.64	0.28
MgO	0.00	0.18	0.64	0.07	0.06	0.46
ZnO	0.80	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.01	0.00	0.00	0.04	0.00
NiO	0.02	0.00	0.03	0.06	0.00	0.05
Total	97.46	100.54	98.67	99.38	99.11	98.10
Formula 6(O)						
Si	0.006	0.006	0.000	0.005	0.000	0.005
Ti	1.499	1.514	1.437	1.463	1.310	0.931
Al	0.001	0.096	0.039	0.075	0.435	0.171
Cr	0.000	0.002	0.005	0.002	0.001	0.002
Fe ³⁺	1.318	1.168	1.430	1.319	1.265	3.808
Fe ²⁺	1.612	1.629	1.573	1.618	1.411	0.014
Mn	0.007	0.003	0.002	0.004	0.042	0.042
Mg	0.000	0.014	0.054	0.006	0.006	0.000
Zn	0.049	0.000	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.000	0.000	0.000	0.002
Ni	0.001	0.000	0.001	0.003	0.000	0.005
Total *	4.494	4.431	4.541	4.494	4.471	4.977
ΣR ²⁺	1.668	1.646	1.630	1.630	1.459	1.512
ΣR ³⁺	2.825	2.785	2.911	2.864	3.012	3.465
%Ilmenite	53.1	54.4	49.4	51.1	24.0	29.9
%magnetite	6.8	6.9	8.3	9.5	40.0	34.5
%hematite	38.7	33.7	39.8	35.5	35.5	37.9

Note: * previously reported by Vu et al. [9]. Fe²⁺ and Fe³⁺ were recalculated from total FeO after the method of Droop [26]. ΣR²⁺ = Fe²⁺ + Mn + Mg + Zn + Ca + Ni. ΣR³⁺ = Si + Ti + Al + Cr + Fe³⁺.

Ilmenite inclusions yielded EPMA analyses, as summarized in Table 3. Their compositions ranged from about 34–37% TiO₂, 61–64% FeO, and ≤1.5% Al₂O₃. However, two ilmenite inclusions (GL25 and GL86) in Pleiku sapphire show higher Fe contents (75–76% FeO) with lower Ti contents (19–20% TiO₂). Ternary plots of the FeO–Fe₂O₃–TiO₂ system (Figure 10) showed clearly that most ilmenite inclusions fall within ilmenite–hematite series in which GL25 and GL86 samples move towards the hematite component. Consequently, their recalculated atomic proportions yielded different end-member ratios of ilmenite–hematite–magnetite as Il_{24–30}He_{36–38}Mt_{35–40} and Il_{49–54}He_{34–40}Mt_{7–10}, which can be grouped into titanomagnetite and titanohematite, respectively (Table 3).

5. Discussion

5.1. Classification of Iron Oxide Inclusions

Based on morphological and Raman spectroscopic characteristics combined with EPMA analyses, iron oxide minerals in sapphire from Southern Vietnam can be grouped into wüstite, hercynite, and ilmenite. These EPMA analyses are newly reported for the mineral chemistry of these oxide inclusions in sapphires from Southern Vietnam.

This is the first report of wüstite found as an inclusion in gem sapphire. Its composition, Fe_{1–x}O with 0.04 < x < 0.12, should be stable at < 570°C and can be transformed between α-Fe and Fe₃O₄ [31]. As reported above, low power laser (0.5 mW) excitation can decrease alterations on the wüstite surface and then generate a Raman spectrum very

similar to the pattern of magnetite (Fe_3O_4) (Figure 6a). This indicates that the structure of wüstite is made up of non-equivalent sites, called non-stoichiometric wüstite (FeO), because the structure of non-equivalent sites of non-stoichiometric wüstite is similar to that of magnetite (Fe_3O_4) [32]. However, this spectrum changes to a strong decrease in half-intensity peak positions of the magnetite structure (Fe_3O_4) and clearly displays new peaks of hematite structure (Fe_2O_3) plus a peak at 595 cm^{-1} attributed to wüstite, as noticed by Hanesch [23] (Figure 6b) at high laser power (5 mW). This effect supports that wüstite's surface with a magnetite structure might be transformed into a hematite structure by the activation of high laser power. The irreversible transformation of magnetite to hematite caused by a lowering of the temperature in the natural process is commonly known as matitization [33]:

Besides, a strong increase in the peak around 667 cm^{-1} (magnetite) at high laser power was visible in the other wüstite inclusions (Figure 6c), which may be attributed to the Raman active vibrations of spinel groups [27], indicating more spinel components in the structure. They are comparable to the EPMA analyses that yielded non-stoichiometric wüstite (FeO) and wüstite–hercynite (Table 1). The hercynite component (e.g., 23 percent in sample PT49) obtained in non-stoichiometric wüstites (Table 1) should affect the intensity of such a magnetite peak (Figure 6c).

Raman spectroscopic features of hercynite spinel inclusions clearly belong to the spinel group. Additionally, EPMA analyses yielded the composition of hercynite (Table 2 and Figure 9).

Figure 9. Compositional plots of hercynite spinel inclusions in sapphires from Southern Vietnam. This diagram was suggested by Haggerty [34].

Raman spectroscopic features of ilmenite inclusions only exhibited the mixture patterns of ilmenite and hematite, called ilmenite solid solutions. In addition, the broadened peaks at 399 , 600 , and 1298 cm^{-1} of hematite (Figure 8b) were caused by the oxidation of titanomagnetite. This oxidation seems to be influenced by ilmenite exsolution in the Ti-rich magnetite (titanomagnetite) which was reported previously in igneous intrusive from Bijigou, Pazhihua, and Xinjie in China [35]. Meanwhile, the EPMA analyses of ilmenite solid solutions clearly defined titanohematite and titanomagnetite (Table 3 and Figure 10).

Figure 10. Ternary FeO–Fe₂O₃–TiO₂ diagram and plots of ilmenite–hematite inclusions in sapphire from Southern Vietnam. The diagram was suggested by Buddington and Lindsley [1].

From the results, Raman spectroscopic features of ilmenite inclusions clearly exhibited ilmenite solid solutions (e.g., ilmenohematite and titanomagnetite), which are characteristic of rhombohedral solid solutions [25]; on the other hand, hercynite spinel and wüstite have cubic and octahedral shapes [30]. The EPMA shows attributes of wüstite and hercynite in octahedral iron oxide inclusions, whereas rhombohedral iron oxides favor ilmenite–hematite (titanohematite and titanomagnetite). The morphological characteristics of the iron oxide minerals in sapphire from Southern Vietnam match the results of Raman and EPMA analyses.

5.2. Crystallization Environment

Iron oxide inclusions in sapphire from Southern Vietnam are mostly characterized by euhedral crystals (rhombohedral and octahedral) which appear to be primary inclusions [36]. Therefore, their chemical and physical conditions can be used to reconstruct the crystallization environment of the host sapphire.

Non-stoichiometric wüstite appears to have formed under a strongly reducing condition [29,37]. Furthermore, the co-existing wüstite and hercynite inclusions in sapphire from Southern Vietnam (Figure 5) may be involved by the hercynite's breakdown reaction process [38,39]:

Therefore, cogenetic wüstite and hercynite inclusions should be formed in a strongly reducing environment related to the hercynite breakdown reaction process. On the other hand, titanomagnetite and titanohematite inclusions should be generated by sub-solidus re-equilibration [1,40] which suggests an oxidizing environment. The compositions of titanomagnetite inclusions vary towards hematite components without ulvöspinel components (Table 3) which should be re-equilibrated under the slow cooling oxidized sub-solidus environment [1,41]. This supports the complete oxidation reaction of spinel_{ss} by the re-equilibration: $4\text{Fe}_3\text{O}_4 \text{ (in exsolution)} + \text{O}_2 = 6\text{Fe}_2\text{O}_3 \text{ (in ilmenite)}$ to ilmenite exsolution in titanomagnetite.

This information indicates an environmental change during the formation of these oxide inclusions as well as their host sapphire. Initial crystallization should take place in a strongly reducing (indicated by wüstite occurrences) magma chamber prior to the slow cooling sub-solidus stage under a low oxidizing condition (based on phase transformation

from titanomagnetite to titanohematite). This process may be related to oxygen fugacity and temperature changing towards the slow cooling process.

Inclusions and their host sapphire from Southern Vietnam were suggested to have formed in the lower crust [7,9] and in the lithospheric mantle [10]. In this study, wüstite with a cubic shape should be typified by crystallization at a temperature of about 570 °C [31]. This thermal process should be located in the continental crust (≤ 800 °C) [42]. Furthermore, wüstite appears to have occurred in the continental crust, as suggested by Seifert et al. [29], who reported wüstite in fluorapatite crystallized from S-type granite melts. Additionally, hercynite has been recognized in magmatic sapphires also formed in crust [43,44]. In addition, titanomagnetite inclusion with Il_{24-30} components seems to be formed in plutonic rocks under a crustal environment, as suggested by Buddington et al. [45]. Therefore, coexisting wüstite, hercynite, titanohematite, and titanomagnetite clearly indicate that these oxide inclusions and their host sapphire should have crystallized directly from magma in crust instead of mantle.

Under the silica-saturated condition, iron oxide minerals (i.e., wüstite, hercynite, titanomagnetite, and titanohematite) are not stable; all Fe^{2+} atoms preferentially enter silicate structures instead. Therefore, wüstite, hercynite, titanomagnetite, and titanohematite may only be formed in the silica-undersaturated environment. Titanomagnetite indicated a higher temperature (at about 600–700 °C) than the ilmenite–hematite miscibility gap [46]. Titanomagnetite should crystallize directly from magma prior to sub-solidus re-equilibration of iron–titanium oxides during a slow cooling process within a low oxidizing environment. This late state re-equilibration led to a decrease in magnetite in spinel_{ss}, with $f\text{O}_2$ increasing slightly.

6. Conclusions

Iron oxide mineral inclusions provide useful indicators of crystallization conditions of their host sapphire from Southern Vietnam. These iron oxide inclusions include wüstite, hercynite, titanomagnetite, and titanohematite series. Crystal morphology, Raman spectroscopy, and mineral chemical signatures of these iron oxides indicate silica-undersaturated magmatic origin in the lower crust. Wüstite might have crystallized from the hercynite's breakdown reaction (hercynite = sapphire + wüstite), whereas titanomagnetite and titanohematite series should have formed in sub-solidus re-equilibration within the slow cooling process. These results indicate an environmental change during the crystallization process of sapphire, wüstite, and hercynite in the reducing magma chamber prior to a slow cooling sub-solidus re-equilibrium of titanomagnetite to titanohematite with low oxidizing conditions.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2075-163X/11/3/241/s1>, Table S1: Sapphire samples used in this study.

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